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PATENT OFFICE  
DEPARTMENT OF TRADE AND  
INDUSTRY

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Application form P.1 and the provisional specification of South African Patent  
Application No. 2003/8023 as originally filed in the Republic of South Africa  
on 15 October 2003 in the name of ESKOM HOLDINGS LIMITED for an  
invention entitled: "CATALYTIC CONVERSION".

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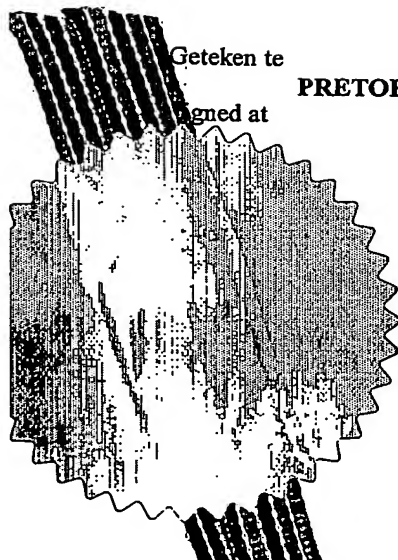
PRETORIA

in die Republiek van Suid-Afrika, hierdie  
in the Republic of South Africa, this

8

dag van  
November 2004  
day of

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REPUBLIC OF SOUTH AFRICA  
PATENTS ACT, 1978  
APPLICATION FOR A PATENT AND  
ACKNOWLEDGEMENT OF RECEIPT  
(Section 30(1) Regulation 22)

REPUBLIC OF SOUTH AFRICA	
FORM P.1	REVENUE
(to be lodged in duplicate)	
15.10.03	R 060.00
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A&A REF: 15/09/03	

THE GRANT OF A PATENT IS HEREBY REQUESTED BY THE UNDERMENTIONED APPLICANT  
ON THE BASIS OF THE PRESENT APPLICATION FILED IN DUPLICATE

21 01 PATENT APPLICATION NO 2003/8023

71 FULL NAME(S) OF APPLICANT(S)

ESKOM HOLDINGS LIMITED

ADDRESS(ES) OF APPLICANT(S)

Megawatt Park, Maxwell Drive, SUNNINGHILL,  
Gauteng Province, Republic of South Africa

54 TITLE OF INVENTION

"CATALYTIC CONVERSION"

Only the items marked with an "X" in the blocks below are applicable.

☐ THE APPLICANT CLAIMS PRIORITY AS SET OUT ON THE ACCOMPANYING FORM P.2. The earliest priority claimed is

Country:

No:

Date:

☐ THE APPLICATION IS FOR A PATENT OF ADDITION TO PATENT APPLICATION NO

21 01

☐ THIS APPLICATION IS A FRESH APPLICATION IN TERMS OF SECTION 37 AND BASED ON  
APPLICATION NO

21 01

THIS APPLICATION IS ACCOMPANIED BY:

- |                                     |  |
|-------------------------------------|--|
| <input checked="" type="checkbox"/> | A single copy of a provisional specification of 15 pages                         |
| <input type="checkbox"/>            | Drawings of sheets   |
| <input type="checkbox"/>            | Publication particulars and abstract (Form P.8 in duplicate) (for complete only) |
| <input type="checkbox"/>            | A copy of Figure of the drawings (if any) for the abstract (for complete only)   |
| <input type="checkbox"/>            | An assignment of invention - To follow   |
| <input type="checkbox"/>            | Certified priority document(s). (State quantity)                                 |
| <input type="checkbox"/>            | Translation of the priority document(s)  |
| <input type="checkbox"/>            | An assignment of priority rights   |
| <input type="checkbox"/>            | A copy of Form P.2 and the specification of RSA Patent Application No            |
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| <input type="checkbox"/>            | Request for ante-dating on Form P.4  |
| <input type="checkbox"/>            | Request for classification on Form P.9   |
| <input type="checkbox"/>            | Request for delay of acceptance on Form P.4                                      |
| <input type="checkbox"/>            | Extra copy of informal drawings (for complete only)                              |

21 01

74 ADDRESS FOR SERVICE: Adams & Adams, Pretoria

Dated this 15 day of October 2003

AV vR SCHWEIZER  
ADAMS & ADAMS  
APPLICANTS PATENT ATTORNEYS

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FORM P6

REPUBLIC OF SOUTH AFRICA  
Patents Act, 1978

## PROVISIONAL SPECIFICATION

(Section 30 (1) - Regulation 27)

21	01	OFFICIAL APPLICATION NO
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22	LODGING DATE
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... 2003 / 8023

15 October 2003

71	FULL NAME(S) OF APPLICANT(S)
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ESKOM HOLDINGS LIMITED

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54	TITLE OF INVENTION
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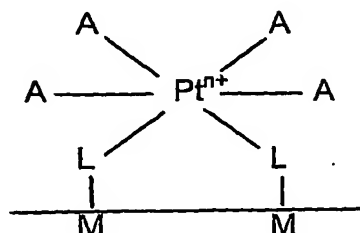
"CATALYTIC CONVERSION"

**THIS INVENTION** relates to catalytic conversion. More particularly, the invention relates to a process for the catalytic conversion of lower alkanes to products selected from the group consisting of alcohols and aldehydes, and to a catalyst for use in the process.

According to the invention there is provided a gas-phase process for the catalytic conversion of a lower alkane comprising at most 5 carbon atoms to products selected from the group consisting of alcohols, aldehydes and mixtures thereof, the process comprising bringing the lower alkane into contact with an oxidizing agent in the presence of a catalyst comprising at least one platinum complex.

The catalyst may be a heterogeneous catalyst wherein the platinum complex is supported on a catalyst support such as a metal oxide catalyst support to whose surface the platinum complex may be chemically bonded. The metal oxide may be selected from the group consisting of alumina ( $\text{Al}_2\text{O}_3$ ), silica ( $\text{SiO}_2$ ), titania ( $\text{TiO}_2$ ), zirconia ( $\text{ZrO}_2$ ) and molybdena ( $\text{Mo}_2\text{O}_3$ ). In particular, the catalyst may be a heterogeneous catalyst in which each platinum complex has two ligands which are

chemically bonded to the surface of the metal oxide catalyst support, and the catalyst may have, for example, the following structure:



In which:

L is selected from amino groups, hydroxyl groups and imidazolyl groups;

A is selected from hydroxyl groups, chloride groups and amino groups;

M is selected from aluminium, silicon, zirconium, titanium and molybdenum; and

n is an integer selected from 4, 2 and 1,

so that the platinum (Pt) has a valence, depending on the numerical value of n, of (IV),

(II) or (I), as the case may be, the platinum being the central atom of the complex, the A

groups and L groups being ligands surrounding the central platinum atom, the L ligands

or groups acting chemically to bond the complex to the metal oxide support surface.

The platinum content of the catalyst, including the support, may be 1 – 6 mg/cm<sup>3</sup>.

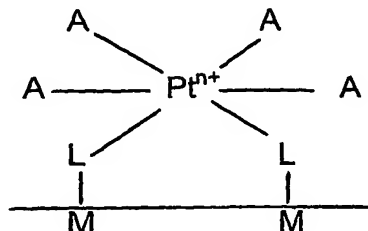
It is expected that the process will be particularly suitable for the direct catalytic conversion of methane to methanol and/or formaldehyde by the partial oxidation of the methane. The oxidizing agent may be oxygen in molecular form (O<sub>2</sub>) optionally as a component of air or of a suitable air/oxygen mixture, the lower alkane

being contacted in the presence of the catalyst with said oxygen, air or air/oxygen mixture.

The process may be carried out at an elevated temperature, for example in the range 60 – 120°C. The pressure at which the process may be carried out is not critical and is conveniently atmospheric pressure. Typically, the process will be carried out in a reactor in which the supported catalyst is contained and over which catalyst a reaction mixture, comprising the alkane or alkanes to be converted and the oxidizing agent, is passed under the above reaction conditions, conveniently at a space velocity of 2 – 20cm<sup>3</sup> reaction mixture/cm<sup>3</sup> reactor volume/minute.

The catalyst support may be porous and may be in tubular- or flat sheet form, being fixed in the interior of the reactor, the reaction mixture being passed through and over the catalyst and support in the reactor. In particular the catalyst support may comprise a plurality of said metal oxides as components thereof, being, for example, a bi-component or multi-component mixture to said metal oxides. In this regard it is to be noted that the present specification regards silica (Si) and molybdenum (Mo) to be metals. Furthermore, the catalyst support may comprise, in addition to said metal oxides, additional components such as aluminosilicates, zeolites, porous ceramic oxides, fibrous oxides, and other bi-component and multi-component metal oxides.

The invention extends to a catalyst comprising a platinum complex supported on a metal oxide support and having said structure:

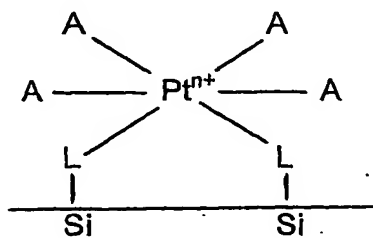


In which L, A, M and n are as hereinabove defined, the central platinum atom having a valence n of (IV), (II) or (I) and the platinum being present in the form of a metal complex, two ligands of which are chemically bonded to the surface of a support, which is an oxide of the metal M.

The invention extends further to a product, in particular an alcohol or an aldehyde, whenever produced by the process described and defined above.

The catalyst of the present invention comprises polyvalent platinum as a component of a poly-ligand complex bonded to a metal oxide surface. Platinum can be present in three oxidation states. Without being bound by theory, it is believed that, during the alkane oxidation process, Pt (IV) is reduced to Pt (II) and possibly also to Pt (I). Simultaneously with alkane oxidation, the oxygen from the oxidizing agent (air and/or oxygen) present in the reaction mixture re-oxidizes the platinum, thus returning it to the highest oxidation state (IV).

The catalyst of the present invention comprises the platinum complex bonded to the metal oxide surface, which acts as a catalyst support. Two ligands of the platinum complex are chemically bonded to surface metal atoms of the support. The structure of one of the more active platinum complexes, attached to the surface of silica, is shown below:



In this complex, L is an amino group or a hydroxyl group, A is a hydroxyl group or a chloride group, M is silicon and n is 4.

According to the mechanism discussed above, platinum in the surface complex is present in the valence state of (IV).

The catalyst of the present invention consists of the platinum metal complex chemically bonded to the surface of the support. Suitable supports include the abovementioned oxides of aluminium, silicon, titanium, zirconium, molybdenum and optionally also the abovementioned other suitable metal oxides and mixtures thereof,



such as aluminosilicates, zeolites, porous oxides, fibrous oxides, bi-component mixed oxides and multi-component mixed oxides.

Preferred supports are manufactured from porous metal oxides and are in the form of flat sheets or tubes. Fibrous and globular ceramic materials containing oxides of each of silicon, aluminium and zirconium can be used as starting materials for porous support preparation. The porous structure of the support can be modified by introducing additional ceramic material comprising one of the metal oxides mentioned above into a near-surface layer of the support. Platinum-containing complexes can then be attached to the support surface.

A platinum content in the catalyst is employed of 1 – 6 mg platinum/cm<sup>3</sup> catalyst, preferably 3 – 6 mg/cm<sup>3</sup>. The most preferable platinum content is about 3 mg/cm<sup>3</sup>. It is believed that a content of about 3 mg/cm<sup>3</sup> allows for an even distribution of platinum on the catalyst surface and in its porous interior.

The process described in the present application is conveniently carried out in thermally-controlled reactors (reactor vessels) made of stainless steel. The interiors of the reactors constitute reaction zones which are partitioned by flat-sheet and/or tubular porous catalyst elements. Reaction mixtures containing selected quantities of selected alkanes and air and/or oxygen at selected temperatures and pressures are passed through the porous supports in the reaction zones and are then

removed from the reactions zones. The condensible reaction products (water, alcohols, aldehydes and carbon dioxide) can be investigated chromatographically.

The benefits of using porous catalytic elements in the flat-sheet or tubular form in the reactors are as follows:

- (a) Reduction of reaction rate-limiting factors, such as diffusion of the reaction mixture into catalyst particles, which diffusion plays an important role in conventional fixed-bed granular catalytic systems;
- (b) Decrease in the contact time between the reaction mixture and the catalyst; and
- (c) Reduction of the possibility of complete alkane oxidation to carbon oxides such as carbon monoxide or carbon dioxide, thus increasing the alcohol and aldehyde selectivity of the process.

Under the conditions described above, the time of contact between the catalyst and the reaction mixture is determined by the velocity of gas flow through the ceramic catalytic elements.

The invention will now be described, by way of non-limiting illustrative example, with reference to the following experiments and with reference to the accompanying Tables, for the catalytic conversion, according to the process of the

present invention, of methane to methanol and aldehyde, carried out in the gas phase. The reaction temperature was in the range 30 – 180°C, preferably 60 – 120°C, the most preferable temperature range being 90 – 120°C. The oxidizing agents were air and/or oxygen. The methane : oxygen molar ratio in the reaction mixture was in the range 3-5: 1. The mixtures with the ration 5 : 1 were the most effective reaction mixtures under the laboratory conditions employed.

Based on the experimental results, it is believed that the reaction mechanism includes reduction of platinum (IV) to platinum (II) and further to platinum (I). In the presence of air or oxygen the catalyst is spontaneously re-oxidized by molecular oxygen (O<sub>2</sub>) to the initial valence state of (IV).

The catalysts which were used are set forth in Table 1, which gives information about catalyst supports, catalyst complexes and platinum content. In Table 2 details of the catalytic activities of the catalysts used in the conversion of methane by oxidation are given. The molar ratio of methane (in natural gas) to oxygen in the reaction mixtures was 3-5 : 1. The reactions were carried out under atmospheric pressure, at various temperatures and rates of reaction mixture flow through the reactors. Flat-sheet and tubular catalyst supports were used.

The catalysts described in the present application were found to be active at temperatures lower than those required for activity of homogeneous catalysts

containing platinum. The main advantages of the catalysts of the present invention were found to be as follows:

- (a) Oxidation by means of the catalytic conversion process was found to be possible in the gas phase;
- (b) No additional reagents other than alkane (methane or natural gas) and oxygen or air were found to be necessary for performing the catalytic conversion;
- (c) Ease of separation of the heterogeneous catalyst from the reaction products was experienced; and
- (d) There was an absence of catalyst contamination of the reaction products.

Changing conditions of the catalytic reaction, the reaction mixture flow rate (residence time) and temperature permitted control of the catalyst selectivity towards the formation of alcohols and aldehydes (methanol and formaldehyde when methane was oxidized) as shown in Table 3. Optimisation of the catalytic process allowed production of either formaldehyde (selectivity 99%) or methanol (selectivity 86%) as main reaction products at methane conversions of 1 – 10%.

Table 4 shows that the catalysts of the present invention possess catalytic activity towards light alkanes other than methane present in natural gas. Conversion of ethane and butane (butane mixed with iso-butane) significantly exceeded that of methane.

The present invention achieves a degree of conversion and methanol selectivity, in the direct oxidation of methane or natural gas by air or oxygen, which is high. The invention permits direct gas-phase oxidation of lower alkanes to alcohols or aldehydes under mild reaction conditions using molecular oxygen or air. No catalytic promoters of any types, e.g. gaseous chlorine or nitrogen oxides, are required for the process.

**TABLE 1: DESCRIPTION OF CATALYSTS**

Catalyst	Support	Complex of Pt	Content of Pt (mg/cm <sup>3</sup> )
1	Fibrous oxides: 47% SiO <sub>2</sub> , 40% Al <sub>2</sub> O <sub>3</sub> , 13% TiO <sub>2</sub>	L = amino, A = Cl	1.08
2	Fibrous oxides: 47% SiO <sub>2</sub> , 46% Al <sub>2</sub> O <sub>3</sub> , 7% TiO <sub>2</sub>	L = imidazolyl, A = Cl	1.27
3	Fibrous oxides: 50% SiO <sub>2</sub> , 42% Al <sub>2</sub> O <sub>3</sub> , 8% Mo <sub>2</sub> O <sub>3</sub>	L = hydroxyl, A = Cl	1.45
4	Fibrous oxides: 48% SiO <sub>2</sub> , 40% Al <sub>2</sub> O <sub>3</sub> , 12% Mo <sub>2</sub> O <sub>3</sub>	L = amino, A = amino	1.45
5	Fibrous oxides: 53% SiO <sub>2</sub> , 40% Al <sub>2</sub> O <sub>3</sub> , 7% TiO <sub>2</sub>	L = imidazolyl, A = amino	2.50
6	Fibrous oxides: 53% SiO <sub>2</sub> , 40% Al <sub>2</sub> O <sub>3</sub> , 7% ZrO <sub>2</sub>	L = hydroxyl, A = amino	3.00
7	Fibrous oxides: 58% SiO <sub>2</sub> , 40% Al <sub>2</sub> O <sub>3</sub> , 2% ZrO <sub>2</sub>	L = amino, A = hydroxyl	3.20
8	Fibrous oxides: 57% SiO <sub>2</sub> , 40% Al <sub>2</sub> O <sub>3</sub> , 3% ZrO <sub>2</sub>	L = imidazolyl, A = hydroxyl	5.90
9	Fibrous oxides: 59% SiO <sub>2</sub> , 40% Al <sub>2</sub> O <sub>3</sub> , 1% Mo <sub>2</sub> O <sub>3</sub>	L = hydroxyl, A = hydroxyl	6.00
10	Fibrous oxides: 47% SiO <sub>2</sub> , 53% Al <sub>2</sub> O <sub>3</sub>	L = amino, A = amino	6.00
11	Fibrous oxides: 40% SiO <sub>2</sub> , 45% Al <sub>2</sub> O <sub>3</sub> , 15% ZrO <sub>2</sub>	L = imidazolyl, A = amino	3.20
12	Tubular porous ceramic: 70% Al <sub>2</sub> O <sub>3</sub> , 30% ZrO <sub>2</sub>	L = amino, A = amino	2.20

**TABLE 2: METHANE OXIDATION ACTIVITY OF DIFFERENT CATALYSTS**

Catalyst	Test Gas	T (°C)	Flow rate, (cm <sup>3</sup> / cm <sup>3</sup> / min)	Conversion of CH <sub>4</sub> (%)	Selectivity (%)		
					CO <sub>2</sub>	CH <sub>2</sub> O	CH <sub>3</sub> OH
1	Natural gas	90	8.0	7.33	0.0	99.1	0.9
2	Natural gas	90	6.7	2.54	0.8	64.2	34.7
3	Natural gas	120	6.7	3.20	2.8	94.0	3.1
4	Natural gas	90	8.0	5.09	0.0	97.0	2.9
5	Natural gas	90	8.0	7.78	0.0	70.1	29.2
6	Natural gas	90	8.0	4.31	0.0	97.6	3.2
		120	8.0	3.26	0.0	95.2	4.5
7	Natural gas	90	8.0	2.51	0.0	12.3	87.5
		120	8.0	4.68	0.0	95.0	5.3
8	Natural gas	90	8.0	0.89	0.0	36.9	63.1
		120	8.0	1.35	0.0	34.6	74.8
9	Natural gas	90	8.0	1.92	0.0	34.6	65.4
10	CH <sub>4</sub>	90	8.0	4.70	0.0	39.5	60.5
11	CH <sub>4</sub>	120	8.0	5.74	0.0	91.6	8.1
12	CH <sub>4</sub>	90	8.0	15.4	4.2	65.7	30.0

**TABLE 3: FINAL TESTS OF VARIOUS CATALYSTS IN THE  
CONVERSION BY PARTIAL OXIDATION OF METHANE AND NATURAL GAS**

Catalyst	Test gas	T (°C)	Flow rate (cm <sup>3</sup> / cm <sup>3</sup> / min)	Conversion of CH <sub>4</sub> ( %)	Selectivity (%)		
					CO <sub>2</sub>	CH <sub>2</sub> O	CH <sub>3</sub> OH
2	Natural gas	60	22.3	0.49	0.0	91.2	8.7
		90		1.54	0.0	82.4	27.3
		120		5.05	0.0	93.0	6.2
		60	11.2	0.12	0.0	87.2	22.4
		90		2.12	0.0	54.8	45.2
		120		3.89	0.0	88.4	11.5
		60	6.7	1.24	0.0	80.8	18.8
		90		2.54	0.8	64.2	34.7
		120		1.89	2.2	82.4	15.4
		60	4.4	1.45	0.5	89.1	10.2
		90		2.34	1.8	86.4	13.5
		120		1.50	5.6	90.0	4.3
		60	11.2	1.35	0.0	63.0	36.7
		90		1.53	0.0	47.5	52.4
		120		2.31	0.0	87.5	12.3
		120	6.7	3.20	2.8	94.0	3.1
10	CH <sub>4</sub>	120	4.4	4.23	8.5	89.4	2.1
		90	22.3	3.62	0.0	99.0	0.0
		120		2.45	0.0	99.0	0.0
		90	11.2	4.01	0.0	83.6	16.4
		120		0.21	0.0	99.0	0.0
		60	8.0	0.54	0.0	86.5	15.4
		90		4.70	0.0	39.5	60.5
		120		4.62	0.0	99.0	0.0
		90	6.7	0.70	0.0	17.6	82.4
		120		5.68	0.0	89.1	10.9
		90	4.4	3.08	0.0	75.9	24.1
		120		4.62	0.0	99.0	0.0
11	CH <sub>4</sub>	60	80	1.76	0.0	99.2	0.0
		90		0.98	0.0	99.5	0.0
		120		5.74	0.0	91.6	8.1
		90	6.7	3.63	0.0	92.3	17.5
		120		1.01	0.0	13.6	86.4
		90	4.4	6.73	0.0	76.3	23.7
		120		3.23	0.0	34.6	65.4
		90	2.2	10.22	0.0	85.9	14.0
		120		6.11	0.0	72.8	23.2



**TABLE 4: CONVERSION OF SOME HYDROCARBONS PRESENT IN NATURAL GAS (% VOL)**

Content in natural gas (% vol)	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>4</sub> H <sub>10</sub>
	90.6	3.0	1.0
Catalyst	Conversion at 90°C (%)		
11(1)	7.3	7.3	52.5
22(3)	2.3	3.3	61.3
18(9)	1.9	3.7	25.1

DATED THIS 15<sup>th</sup> day of OCTOBER 2003



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